

A Preliminary Survey of Surface Microlayer Contaminants in Burrard Inlet, Vancouver, B.C. Canada

Brent Moore and Elizabeth Freyman

British Columbia Ministry of Environment, Lands and Parks

Introduction

For many years marine sediments have been recognized as a sink for a large number of contaminants that enter the marine environment. Over the last three decades, it has also been determined that the surface microlayer of marine waters can also be an area of contaminant concentration, especially for chemicals such as pesticides, metals and chlorinated hydrocarbons (Montague 1992). The surface microlayer, approximately 50 microns thick, is the atmospheric interface with the aquatic environment. Thus, contaminants from atmospheric deposition, as well as those from terrestrial runoff, effluent discharges or spills from vessels, can concentrate in this layer.

Toxins in the surface microlayer can be 100 to 10,000 times higher than in the underlying water column, and can potentially cause significant impacts to the eggs and/or larvae of marine organisms that utilize the microlayer as 'nurseries.' It has also been shown that tidal action can coat intertidal organisms with the microlayer contaminants (Hardy and others 1987).

Monitoring has been conducted previously in areas such as Chesapeake Bay (Batelle 1988) and Puget Sound (PTI 1990), with elevated contaminant levels and direct toxicity measurements being recorded. The Ministry has initiated a preliminary sampling program in Burrard Inlet and other areas of Georgia Strait to determine whether or not microlayer contamination could potentially be impacting on marine life in this area.

Methodology

More than 14 techniques have been used to sample surface microlayers (Hardy 1982). In this preliminary survey, standard glass plates were initially used by placing one side in contact with the water surface, then using a rubber blade, or squeegee, to collect the sample into the appropriate sample collection bottles. This method was difficult to use and appeared to collect much more than the narrow surface microlayer. After conferring with experts, a rotating drum sampler was finally decided upon, with a local supplier (Aqua-Guard) of oil spill skimmers custom-building a unit for the Ministry.

Surface microlayer samples were collected by deploying the floating rotating drum unit off the side of the Ministry's 23-foot aluminum work boat *Tantalus*. The drum rotation was powered by the boat's 12-volt battery. Care was taken to not travel in the recent path of boats, including our own vessel. As well, an effort was made to match the forward speed of the boat with the rotating speed of the drum sampler. The microlayer sample adhered to the drum as it rotated out of the water. Prior to moving back into the water, the drum was scraped with a plastic blade that directed the sample to an attached plastic collection tray. Between samples, both the plastic blade and the collection tray were rinsed with the underlying marine water and then with deionized water. The rotating drum was also rinsed with deionized water. Attempts were made to only collect samples in water conditions that allowed microlayers to remain intact and be readily sampled. Even minor wave action was found to foul the sample in the collection tray, as underlying surface water could splash into the tray.

Microlayer samples were generally collected as composites, as each sample collection took approximately 20 to 30 minutes, with the rotating drum covering approximately 200 square metres of the water surface. Traditional surface water samples were collected directly into the sample bottle, just below the water surface.

Metals samples were collected into acid-rinsed 250 mL plastic bottles, then immediately preserved with 2 mL of Ultra Pure 1:1 nitric acid, and placed in a cooler with ice packs. The shipped samples were received

the next day by ALS Environmental (formerly ASL Analytical Service Laboratories Ltd.) in Vancouver, where metals were analysed using the following approved methods (ALS, 2000):

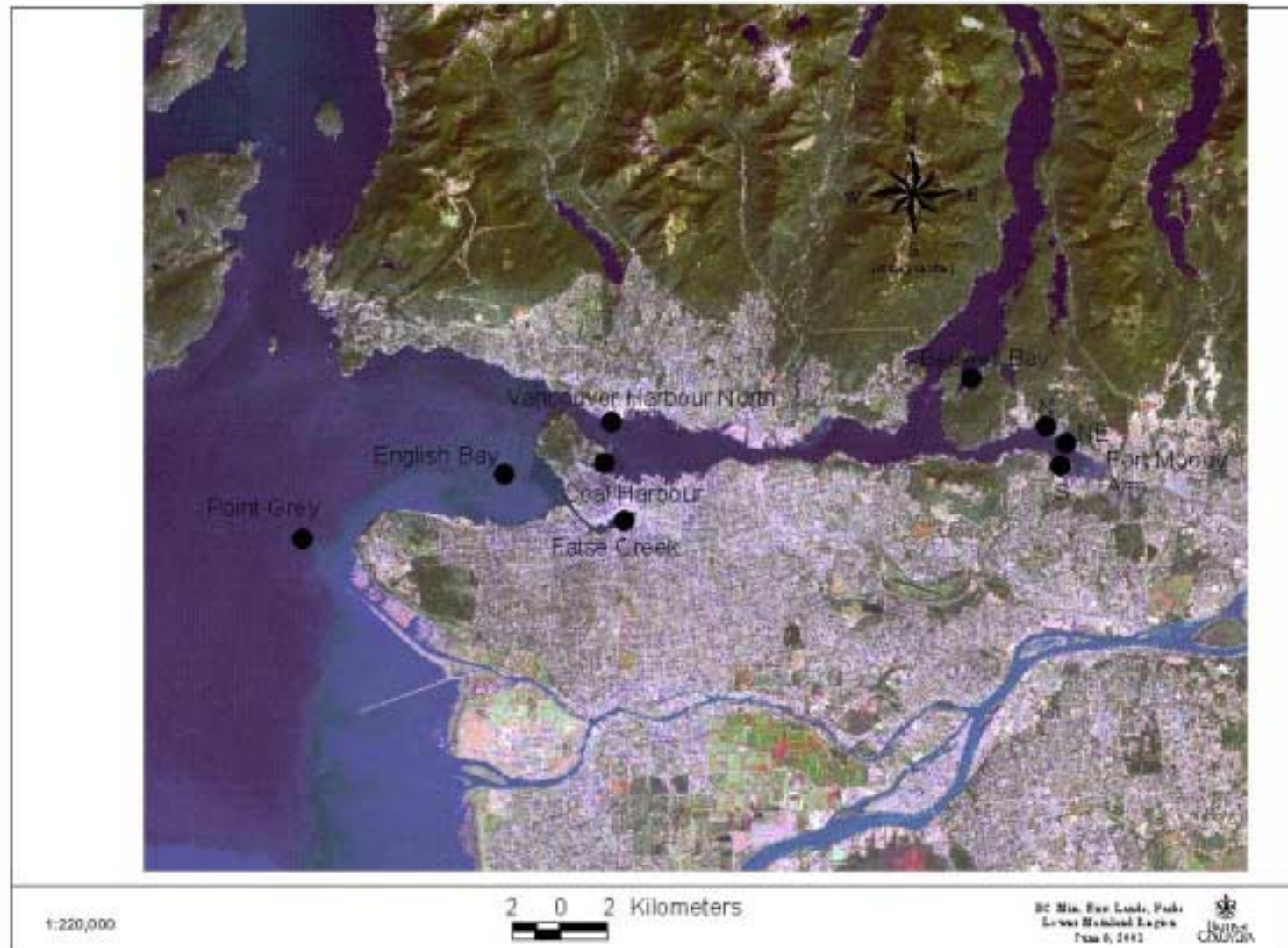
- Trace metals in seawater were analysed by SPR-IDA Chelation, using procedures from “Standard Methods for the Examination of Water and Wastewater”, 20th Edition, 1998, published by the American Public Health Association, and with procedures adapted from Cetac Technologies Incorporated. A suspended particulate resin (SPR), consisting of immobilized iminodiacetate (IDA) on a divinylbenzene polymer, is used to chelate and preconcentrate metals in seawater. Instrumental analysis is by inductively coupled plasma mass spectrometry (ICPMS) and/or routine atomic absorption spectrophotometry techniques (EPA7000 series).
- The mercury in seawater analysis is carried out using procedures adapted from “Standard Methods for the Examination of Water and Wastewater”, 20th Edition, 1998, published by the American Public Health Association, and with procedures adapted from “Test Methods for Evaluating Solid Waste” SW-846 published by the United States Environmental Protection Agency (EPA). The procedure involves a cold oxidation of the acidified seawater sample using bromine monochloride prior to reduction of the sample with stannous chloride. Instrumental analysis is by cold vapour atomic absorption spectrophotometry (EPA Method 747A/7471A).
- The Metals in Filter Media and/or Swabs analysis is carried out using procedures adapted from WCB Methods 1050 and 1051, published by the Worker’s Compensation Board of British Columbia and/or OSHA Methods ID-1212 and ID-125G, published by the Occupational Safety and Health Administration, Salt Lake City, Utah. The procedure involves a hotplate digestion of the filter media or swab material, using either nitric acid or a combination of nitric acid and hydrochloric acid. Instrumental analysis of the filter or swab extract is by atomic absorption/emission spectrophotometry (EPA Method 7000A), inductively coupled plasma-optical emission spectrophotometry (EPA Method 6010B), and/or inductively coupled plasma-mass spectrometry (EPA Method 6020).

Polycyclic Aromatic Hydrocarbon (PAH) samples were collected into a certified clean 1 Litre brown glass jar for organics analysis. The sample bottles were then placed, unpreserved, in a cooler with ice packs, and delivered the next day to Environment Canada’s Pacific Environmental Science Centre (PESC) in North Vancouver for analysis. PESC prepared the samples using a dichloromethane extraction and concentration to less than 1 mL volume. The analysis was then conducted using a gas chromatography/mass spectrometry (GC/MS) method in Selected Ion Monitoring (SIM) mode. (McPherson, 2001)

Microtox® samples were collected into 250 mL plastic bottles that were immediately placed, unpreserved, into the sample cooler with ice packs. The shipped samples were received the following day by PESC. As results equivalent to ‘acute toxicity’ were not expected in the ambient environment, the reporting focus was placed on the 100% Screen Test Results. Materials and methods followed Environment Canada, Biological Test Method: Toxicity Test Using Bioluminescent Bacteria, Report EPS 1/RM/24 November 1992 and standard Microbics procedures (December 1992 Updated Manual for Microtox® testing). (Buday 2000).

Sampling stations were set out in Burrard Inlet as shown on Figure 1. A local background site was established in Bedwell Bay, part of the relatively undeveloped Indian Arm. Expected impact stations were then set in Vancouver Harbour, including Coal Harbour, and in Port Moody Arm. In 1999, an additional background site was set off Point Grey, in Georgia Strait, and additional impact stations were sited in False Creek and English Bay.

Figure 1: Burrard Inlet Microlayer Stations



Results

Microlayer sampling in Burrard Inlet was first conducted in 1999, but results were not reported due to sampling inconsistencies (including variations in weather, wave action, analyses requested, and use of the rotating drum). While our limited Howe Sound, Malaspina Strait and Okeover Inlet 1999 microlayer sampling results were also not reported due to start-up problems, some general trends were apparent even in the limited data sets. In the microlayer of all three waterbodies, 1999 dissolved copper, lead and zinc levels were from 15% to 700% greater than those levels in the underlying water column. The microlayer contaminant levels were also highest at stations nearest the study area's largest point sources for both air emissions and effluent discharges. In addition, the Microtox® 100% Screen Test Results with these microlayer samples showed a significant elevation in percent light reduction (or 'toxicity') with the test bacteria over those recorded with the underlying water samples. A similar trend was observed with the 1999 Microtox® test results from Burrard Inlet.

The sample collection and equipment handling techniques of 1999 were resolved prior to the 2000/01 sampling year. On October 12th and 20th, 2000, two field sampling trips were conducted to collect microlayer samples in Burrard Inlet. Metals results are shown in Table 1 below. Data from field-preserved Travel Blanks, Rotating Drum Deionized Water Rinse, Method Blanks, and Reference Material comparisons (ALS, 2000) are available upon request. Additional microlayer and underlying water samples were collected from the Coal Harbour area on October 12, 2000 for Extractable ('Total'), Dissolved and Particulate Metals levels; the results are shown in Table 2. PAH results are shown in Table 3, while the Microtox® 100% Screen Test Results are shown in Table 4.

Table 1. Metals Levels in Surface Microlayer and Underlying Water Samples from Burrard Inlet

Microlayer Station	Parameter (ug/L)								
	Hg	Cd	Co	Cu	Pb	Mn	Ni	U	Zn
October 12, 2000									
Coal Harbour	0.09	0.11	0.44	42.6	9.13	27.7	3.09	1.36	34.6
Underlying Water	<0.05	0.05	0.06	2.82	1.01	8.34	0.37	1.63	6.7
Pt. Moody Arm S	<0.05	0.06	0.06	2.96	0.52	8.67	0.49	1.87	6.5
Underlying Water	<0.05	0.06	<0.05	0.96	0.12	7.96	0.35	1.89	3.4
Van. Harbour North	<0.05	0.12	0.07	38.6	6.54	7.41	0.54	1.88	22.1
Underlying Water	<0.05	0.09	0.05	2.31	0.38	7.18	0.42	2.11	10.4
Bedwell Bay	<0.05	0.05	<0.05	4.98	0.92	2.10	0.30	1.45	3.7
Underlying Water	<0.05	0.04	<0.05	0.57	0.06	1.72	0.25	1.54	1.0
October 20, 2000									
Pt. Moody Arm NE	<0.05	0.20	0.12	3.06	1.98	18.9	0.75	0.93	7.2
Underlying Water	<0.05	0.04	0.11	0.94	1.24	21.6	0.44	0.76	4.0
Pt. Moody Arm N	<0.05	0.19	0.64	10.8	7.66	86.9	3.54	0.86	43.7
Underlying Water	<0.05	0.03	0.07	0.82	0.48	10.8	0.40	0.83	3.5
Ministry Criteria	<0.02*	.1max	-	2 ave.	2 ave.	100	8.3ave.	100	10

Ministry criteria exceedances are shown in bold. "ave." = average criterion, "max" = maximum criterion.

*Mercury criterion is based upon methylmercury content.

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Table 2. Total, dissolved and particulate metals levels in Burrard Inlet surface microlayer and underlying surface waters.

Sample	Parameter (ug/L)								
	Hg	Cd	Co	Cu	Pb	Mn	Ni	U	Zn
Microlayer									
Total Metals	<0.05	0.09	0.13	11.2	1.1	18.3	2.15	1.08	24.2
Dissolved Metals	<0.05	0.09	0.13	7.95	0.13	17.8	1.43	1.08	23.0
Particulate Metals	<0.05	<0.03	<0.05	3.12	0.97	0.51	0.72	<0.05	1.2
Underlying Waters									
Total Metals	<0.05	0.05	<0.05	2.54	0.43	3.67	1.05	1.57	8.4
Dissolved Metals	<0.05	0.05	<0.05	1.77	0.05	2.96	0.41	1.57	6.0
Particulate Metals	<0.05	<0.03	<0.05	0.77	0.38	0.71	0.64	<0.05	0.8
Ministry Criteria	<0.02*	.1max.	-	2 ave.	2 ave.	100	8.3ave	100	10

Ministry criteria exceedances are shown in bold. "ave." = average criterion, "max." = maximum criterion.

*Mercury criterion is based upon methylmercury content.

Table 3. Polycyclic Aromatic Hydrocarbons in surface microlayer and underlying water samples from Burrard Inlet.

Parameter		Coal Harbour		Van. Harbour North		Pt. Moody Arm South		Pt. Moody Arm Northeast		Pt. Moody Arm North		Bedwell Bay Control	
		Micro Layer	Under Lying Water	Micro Layer	Under Lying Water	Micro Layer	Under Lying Water	Micro Layer	Under Lying Water	Micro Layer	Under Lying Water	Micro Layer	Under Lying Water
PAH (ug/L)	Safety Level												
Acenaphthene	6	0.02	<.02	<.02	<.02	<.02	<.02	.019	.015	.081	.006	<.02	<.02
Acena-phthylene		0.03	<.02	<.02	.001	<.02	<.02	.015	.004	.19	.005	<.02	<.02
Anthracene		0.08	<.02	<.02	<.02	<.02	<.02	.009	.005	.58	<.02	<.02	<.02
Benzo(a)anthracene		0.26	<.02	<.02	<.02	<.02	<.02	.043	.008	11.1	.016	<.02	<.02
Benzo(a)pyrene	0.01	0.22	<.02	<.02	<.02	<.02	<.02	.025	.003	3.87	<.02	<.02	<.02
Benzo(b)fluoranthene		0.46	<.02	<.02	<.02	<.02	<.02	.054	.006	17	.01	<.02	<.02
Benzo(g,h,i)perylene		0.19	<.02	<.02	<.02	<.02	<.02	.039	.004	3.21	.005	<.02	<.02
Benzo(k)fluoranthene		0.36	<.02	<.02	<.02	<.02	<.02	.03	.004	9.06	.01	<.02	<.02
Chrysene	0.1	0.78	.004	.01	<.02	.013	<.02	.084	.015	19.3	.02	.006	<.02
Debenz(a,h)anthracene		0.05	<.02	<.02	<.02	<.02	<.02	.015	<.02	1.31	<.02	<.02	<.02
Fluoranthene		1.34	.013	.041	.004	.023	.004	.061	.014	16	.03	.015	<.02
Fluorene	12	0.03	<.02	<.02	<.02	>.004	<.02	.024	.016	.13	.003	<.02	<.02
Indeno(1,2,3-cd)pyrene		0.2	<.02	<.02	<.02	<.02	<.02	.025	<.02	3.26	<.02	<.02	<.02
Naphthalene	1	0.03	<.02	<.02	<.02	<.02	<.02	.23	.009	<.02	<.02	<.02	<.02
Phenanthrene		0.2	<.02	<.02	<.02	<.02	<.02	.065	.019	1.29	<.02	<.02	<.02
Pyrene		0.71	.006	.026	.014	.014	.001	.13	.045	17.6	.048	.01	<.02

Standard PESC minimum detection limit is 0.02 ug/L for PAHs. They agreed to report detectable levels to 0.001 ug/L, and altered their sample preparation accordingly.

Ministry criteria exceedances are shown in bold.

Table 4. Microtox® 100% Screen test results for microlayer and underlying water samples from Burrard Inlet.

Microtox® Test	Coal Harbour		Van. Harbour North		Pt. Moody Arm South		Pt. Moody Arm Northeast		Pt. Moody Arm North		Bedwell Bay Control	
	Micro Layer	Under Lying Water	Micro Layer	Under Lying Water	Micro Layer	Under Lying Water	Micro Layer	Under Lying Water	Micro Layer	Under Lying Water	Micro Layer	Under Lying Water
5 minute light decrease (%)	2.1	0	1.5	1.5	0	0	9.06	1.09	25.95	0	0	0
15 min. light decrease (%)	3.7	1.1	2.1	1.4	0.5	0	11.74	1.62	32.64	0	0	0

Discussion

In this preliminary Burrard Inlet survey, metals levels measured in the microlayer have been consistently greater than those measured in the underlying surface waters. In the underlying surface waters, Ministry criteria levels were only exceeded for copper (twice, by 16% and 41%) and zinc (once, by 4%). In the microlayer, however, exceedances for copper (six times, by 48%, 53%, 149%, 440%, 1830% and 2030%) and zinc (three times, by 121%, 246% and 337%) are joined by exceedances for mercury (once, by over 350%), cadmium (four times, by 10%, 20%, 90% and 100%) and lead (three times, by 227%, 283% and 357%). As the levels found to impact on sensitive organisms are typically 10 times—or 900% greater than—the criteria—it appears that the more severe exceedances for copper may represent actual impacts to local marine life forms. This conclusion is accentuated when additive or synergistic impacts with the other metals are considered.

The limited characterization of the total, dissolved and particulate metals compartments shown on Table 2 suggests that most microlayer metals reported in this study appear to be in the dissolved form. Only copper and lead appeared to have any significant portion in the particulate form. This data may be useful in determining the relative significance of atmospheric deposition compared to runoff, effluent and spill-related sources. Similarly, ratios of specific PAHs may also assist in determining whether the PAH source is petroleum input as opposed to pyrolytic or combustion sources (Budzinski and others 1997).

Exceedances of PAH criteria are only recorded in the microlayer, with three of six samples exceeding the benzo(a)pyrene criterion (by 150%, 2100% and 38,600%), and two of six samples exceeding the chrysene criterion (by 680% and 19,200%). As with the metals, it appears that the most excessive PAH criteria exceedances noted here represent actual impacts to marine life forms.

The Microtox® data also shows that greater stress on marine life forms is related more to the microlayer contaminant levels than to those levels in the underlying water column. On average, the microlayer 100% Screen Test results are 12 to 15 times the light reduction (or stressing) seen in the underlying water test results. The unreported 1999 data reflects a similar trend.

Further monitoring in the Burrard Inlet microlayer could assist us in better characterizing the significance of microlayer contaminant elevations. *In situ* toxicity testing would also help in determining the actual impact to aquatic life forms. At this time additional microlayer monitoring in Burrard Inlet is underway.

The 1999 unreported data suggests that contaminant elevations of concern, such as those seen in Burrard Inlet, may only be apparent in areas of Georgia Strait that are adjacent to large developed areas. However, localized microlayer impacts may also occur throughout Georgia Strait adjacent to smaller towns, where stormwater and effluent discharges, coupled with vessel sources, may cause limited impacts. Further monitoring is required to determine whether microlayer impacts are restricted to:

- Waterbodies (such as Burrard Inlet) adjacent to major development areas, and/or
- Immediate discharge zones around point sources.

At this time, water quality criteria for the entire water column are being utilized to assess microlayer water quality. As duration of exposure and early life stage sensitivities are significant factors in determining the acceptable levels of contaminants, criteria generally designed for the protection of marine life forms throughout the water column may not be appropriate for the microlayer. Further work is also required in this area.

Summary

The surface microlayer of waterbodies has been recognized as an area of significant environmental value, as the eggs and/or larvae of some marine organisms utilize it as a 'nursery.' The microlayer has also been identified as a site of contaminant concentrations, with the major contaminant sources including stormwater and effluent discharges, spill events, and atmospheric deposition. Microlayer contamination has been characterized in other jurisdictions, such as Puget Sound and Chesapeake Bay. In 1999 and 2000, the Ministry undertook microlayer sampling in areas of Georgia Strait, including Burrard Inlet. Results indicate that contaminant elevations do occur in the Burrard Inlet microlayer, at levels similar to those reported elsewhere. Metals, especially copper, are up to 20 times their criteria in the microlayer, and some PAHs, such as benzo(a)pyrene, are almost 400 times their criteria. These microlayer elevations are also significantly greater than the concentrations measured in the underlying surface waters, which have traditionally been monitored to determine water quality conditions. Thus, a lack of microlayer monitoring may downplay the actual impacts of contaminants to water quality and marine life forms.

The limited sampling suggests that microlayer contamination may be restricted to areas immediately surrounding point sources, or to embayed areas that are adjacent to developed lands, that can provide non-point sources of atmospheric deposition and/or runoff. At this time it is not expected that significant microlayer contamination extends over large areas of Georgia Strait. It is recognized, however, that further monitoring is required in the Strait to accurately characterize the environmental significance of microlayer contamination.

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